

SPECIFICATION

COMPOSITE OXIDE HAVING OXYGEN ABSORBING AND DESORBING
CAPABILITY AND METHOD FOR PREPARING THE SAME

5 Field of Art

The present invention relates to a composite oxide
having particularly excellent oxygen absorbing and
desorbing capability and useful as a co-catalyst for a
catalyst for purifying exhaust gases and as functional
10 ceramics, and a method for preparing the same.

Background Art

A large amount of cerium oxide has conventionally been
used as a co-catalyst for a catalyst for purifying exhaust
gases, ceramics, and the like. In the field of catalysts,
15 for example, properties of cerium oxide, which absorbs
oxygen under the oxidizing atmosphere and desorbs oxygen
under the reducing atmosphere, are utilized for
improving the efficiency in purifying exhaust gases
containing HC/CO/NO_x as its components. In the field
20 of ceramics, the cerium oxide is used in the form of a
mixture or a compound with other elements as electrically
conductive ceramics such as solid electrolyte, taking
advantage of characteristic properties mentioned above.

However, though the conventional oxide mainly

composed of cerium oxide has certain oxygen absorbing and desorbing capability, it cannot exhibit the capability sufficiently at about 600 °C. Further, at a temperature as high as 700 °C or higher, the performance
5 of the oxide is deteriorated.

In order to overcome such drawbacks, there is proposed a composite oxide mainly composed of cerium and zirconium. There are known, for example, a composite oxide containing cerium and zirconium (Japanese Laid-open
10 Patent Application No. 4-334548), cerium dioxide containing zirconium having a large specific surface area prepared by adding 1 to 20 weight % zirconium oxide to cerium oxide (Japanese Patent Publication No. 6-74145), and a cerium-zirconium composite oxide
15 exhibiting the oxygen absorbing and desorbing capability of 100 $\mu\text{mol/g}$ or more at 400 to 700 °C (Japanese Laid-open Patent Application No. 5-28672).

As a further improvement of the above-mentioned composite oxides, there is also proposed a composite
20 oxide containing a third element in addition to cerium and zirconium. Examples of such composite oxide include, for example, a composite oxide composed of cerium, zirconium, and lanthanum (Japanese Laid-open Patent Application No. 6-154606), and a composite oxide

containing cerium oxide, zirconium oxide, and hafnium oxide (Japanese Laid-open Patent Application No. 7-16452).

The conventional composite oxide containing cerium, however, is low in the degree of solid solution in the crystal phase. Further, a composite oxide is not known which can be reduced sufficiently under the reducing atmosphere at a temperature as low as 600 °C. Accordingly, development of a composite oxide containing cerium oxide which exhibits sufficient oxygen absorbing and desorbing capability at low temperatures is demanded.

The conventional composite oxide containing cerium is generally prepared, for example, by a process including the steps of preparing a nitrate solution or a chloride solution containing cerium ions as well as zirconium ions, lanthanum ions, and hafnium ions which are necessary for composition; adding oxalic acid or an alkali compound such as ammonium bicarbonate to the solution to precipitate the metals mentioned above as a composite salt; and calcining the resulting precipitate. It is commonly known that the cerium ions used in the preparation of the composite oxide are trivalent cerium ions unless otherwise mentioned. The

reason for this fact is explained, for example, in
Inorganic Chemistry, New Edition, Volume 1, Toshizo
Chitani, Sangyo Tosho Kabushiki Kaisha, p311 (1959).
According to this reference, solutions of tetravalent
5 cerium salts are prone to be oxidized very easily, and
chlorides of tetravalent cerium easily release chlorine
to become chlorides of trivalent cerium. Thus,
solutions of cerium salts are stable when the cerium ions
are trivalent, and therefore tetravalent cerium salts
10 and solutions thereof are not usually marketed.

It is conventionally known that tetravalent cerium
salts and solutions thereof can be obtained in the form
of nitrates, sulfates, or composite salts of ammonium
nitrates in the process of cerium purification, though
15 such salts are unstable. However, it is not known widely
to use the tetravalent cerium salts and the solutions
thereof.

Disclosure of the Invention

It is an object of the present invention to provide
20 a novel composite oxide which exhibits excellent oxygen
absorbing and desorbing capability particularly at low
temperatures, and which can be used as a co-catalyst for
a catalyst for purifying exhaust gases and as functional
ceramics.

It is another object of the present invention to provide a method for easily preparing a composite oxide of which degree of solid solution is not lower than 70 %, and which exhibits excellent oxygen absorbing and desorbing capability even at low temperatures.

According to the present invention, there is provided a composite oxide having oxygen absorbing and desorbing capability comprising 90 to 100 weight % total of cerium, zirconium, and hafnium based on a total amount of metals contained in the composite oxide, the total amount of cerium, zirconium, and hafnium consisting of 14.0 to 70.5 at% cerium, 29.49 to 72.5 at% zirconium, and 0.01 to 13.5 at% hafnium, wherein degree of solid solution of said composite oxide is not lower than 70 %, and wherein said composite oxide has reducing property that not less than 90 % of tetravalent cerium contained in the composite oxide is reduced into trivalent cerium when the composite oxide is held at 600°C under a reducing atmosphere.

According to the present invention, there is further provided a method for preparing the composite oxide mentioned above comprising the steps of:

(a) precipitating a composite salt from a starting material solution containing cerium ions, zirconium ions, and hafnium ions, 85 to 100 weight % of said cerium ions

contained in the starting material solution being
tetravalent,

(b-1) subjecting said precipitated composite salt to
oxidizing calcination under an oxidizing atmosphere to
5 obtain an oxidized, calcined product, and

(b-2) subjecting said oxidized, calcined product at
least once to reducing calcination followed by oxidizing
calcination (sometimes referred to as the first method
hereinbelow).

10 According to the present invention, there is further
provided a method for preparing the composite oxide
mentioned above comprising the steps of:

(a) precipitating a composite salt from a starting
material solution containing cerium ions, zirconium ions,
15 and hafnium ions, 85 to 100 weight % of said cerium ions
contained in the starting material solution being
tetravalent, and

(b) subjecting said precipitated composite salt at least
once to reducing calcination followed by oxidizing
20 calcination (sometimes referred to as the second method
hereinbelow).

Brief Description of the Drawings

Fig. 1 is a graph showing the relationship between
the reduction ratio of the composite oxide and the amount

of desorbed oxygen.

Fig. 2 is a graph showing the XRD pattern obtained by X-ray diffraction of the composite oxide prepared in Example 1.

5 Fig. 3 is a graph showing the XRD pattern obtained by X-ray diffraction of the composite oxide prepared in Comparative Example 1.

Fig. 4 shows TPR curves obtained by measuring the oxygen desorbing capability of the composite oxides prepared in Example 1 and Comparative Example 1.

Preferred Embodiment of the Invention

The present invention will now be explained in detail hereinbelow.

The composite oxide of the present invention contains,
15 as requisite metals, cerium, zirconium, and hafnium in total of 90 to 100 weight % of the total amount of metals contained in the composite oxide, and specifically the content of each element is 14.0 to 70.5 at%, preferably 40 to 60 at% cerium, 29.49 to 72.5 at%, preferably 39.9
20 to 59.9 at% zirconium, and 0.01 to 13.5 at%, preferably 0.1 to 10 at% hafnium, based on the total amount of the requisite metals, the total of these elements being 100 at%. If the contents of the requisite metals are outside the above range, sufficient oxygen absorbing and

desorbing capability cannot be achieved. In particular, since the valencies of zirconium and hafnium are both constant at 4, the crystal structure of the composite oxide obtained due to the difference between the ion
5 radius of hafnium and that of zirconium is stabilized by adjusting the content of hafnium within the above range.

In the composite oxide of the present invention, other metals may be contained in addition to the requisite
10 metals. Examples of such other metals may include metals such as titanium, tungsten, nickel, copper, iron, aluminum, silicon, beryllium, magnesium, calcium, strontium, and barium; rare earth metals other than cerium; and mixtures thereof. The content of such other
15 metals is less than 10 weight % of the total weight of the metals contained in the composite oxide.

The composite oxide of the present invention has a characteristic structure close to that of the complete solid solution wherein the degree of solid solution, i.e.
20 the content of solid solution in the crystal phase of the composite oxide, is not lower than 70 %, preferably not lower than 75 %. Thus, when the composite oxide is heated under a reducing atmosphere such as in a hydrogen stream, the cerium contained in the composite oxide,

which is tetravalent when the composite oxide is produced,
is easily reduced to become trivalent, thereby forming
a pyrochlore phase ($\text{Ce}_2\text{Zr}_2\text{O}_7$) or a similar crystal phase,
causing excellent oxygen absorbing and desorbing
5 capability. The degree of solid solution may be measured
by the following method.

<Method of Measuring Degree of Solid Solution in
Composite Oxide>

The degree of solid solution in the composite oxide
10 is determined by measuring the lattice parameter of the
composite oxide by X-ray diffraction, and calculating
the ratio of the measured lattice parameter to the
theoretical lattice parameter for a complete solid
solution (This method is described, for example, in X-ray
15 Diffraction Analysis, 95 (1991), Masanori Kato.).
Accordingly, when the crystal structure and the lattice
parameter are already known, the degree of solid solution
may be determined by calculating the spacing of each
lattice plane using a relational expression between the
20 lattice parameter and the exponents, and calculating the
ratio of the measured value to the calculated lattice
spacing. Specifically, first the lattice spacing is
obtained by formula (1) as lattice spacing d_{hkl} on the
(h, k, l) plane of the crystal of the composite oxide.

$$2d_{hkl}\sin \theta = \lambda \quad \cdot \cdot \cdot (1)$$

In the formula (1), λ stands for the wave length of the measuring beam. For example, when an X-ray tube with Cu target is used for providing the measuring beam, λ is 1.54056. In this case, when the formula (1) is solved for d_{hkl} , $d_{hkl}=1.54056/2\sin \theta$ (θ = diffraction angle) is obtained, and the lattice spacing is thus obtained.

On the other hand, when the crystal of the composite oxide is of cubic system, the lattice parameter and the lattice spacing d_{hkl} satisfy the formula (2):

$$1/d_{hkl}^2 = h^2 + k^2 + l^2 / A^2 \quad (A = \text{lattice parameter}) \quad \cdot \cdot \cdot (2)$$

When the formula (2) is solved for the lattice parameter A , $A=(d_{hkl}^2(h^2+k^2+l^2))^{1/2}$ is obtained, and the lattice parameter is thus obtained.

According to X-ray crystallography, Volume I, 307 (1959) Edited by Isamu Nitta, in order for two substances to be mutually dissolved at any ratio to form a substitutional solid solution, the two substances should have similar lattice patterns, following the Vegard's law. Also, the difference in size of the atoms of each substance forming the solid solution is usually less than 15 %. Denoting the lattice parameters of each substance forming the substitutional solid solution by A_1 and A_2 , and the atomic densities thereof by C_1 and C_2 , the lattice

parameter A of the solid solution is obtained by the formula (3):

$$A^n = A_1^n C_1^n + A_2^n C_2^n \quad \cdot \cdot \cdot (3)$$

wherein n is close to 1. In the case of a solid solution
5 of CeO_2 , ZrO_2 , and HfO_2 , since the ion radius of Ce^{4+} is
0.90 Å, that of Zr^{4+} is 0.79 Å, and that of Hf^{4+} is 0.78
Å (Ceramics, Itaru Yasui, 14,927 (1979)), and thus the
difference between the size of a Ce atom and that of a
Zr atom is within 15 %, the Vegard's law mentioned above
10 may be applied. In the cubic system, the lattice
parameter of CeO_2 is 5.41 Å and that of ZrO_2 is 5.07 Å
(Chemical Handbook, Edited by The Chemical Society of
Japan, 1017 (1958)). Substituting the atomic densities
 C_1 and C_2 by 50 mol%, respectively, the theoretical
15 lattice parameter of the complete solid solution of CeO_2
and ZrO_2 is obtained by the formula (3), i.e., $A = 5.41$
 $\text{Å} \times 0.5 + 5.07 \text{Å} \times 0.5 = 5.24 \text{Å}$. In this way, the degree of
solid solution is obtained by calculating the
theoretical lattice parameter for each composition, and
20 obtaining the ratio of the lattice parameter calculated
from the measured value to the theoretical lattice
parameter in percent. The ion radii of Zr^{4+} and Hf^{4+} are
so close that HfO_2 may be regarded as being completely
dissolved in ZrO_2 . In the above case, the theoretical

lattice parameter of ZrO_2 in the cubic system is regarded as the one including HfO_2 in calculating the degree of solid solution.

The composite oxide of the present invention has a characteristically excellent reducing property at low temperatures, that is, not less than 90 %, preferably 93 to 100 % of the tetravalent cerium contained in the composite oxide is reduced to trivalent cerium when the composite oxide is held at 600 °C under a reducing atmosphere such as a hydrogen atmosphere or a carbon monoxide atmosphere. The reduction ratio may be determined by calculating the ratio of the total amount of oxygen desorbed up to 600 °C measured by a method of measuring the oxygen absorbing and desorbing capability to be described below to the theoretical amount of oxygen supposed to be desorbed when 100 % of the tetravalent cerium contained in the composite oxide is reduced into trivalent cerium.

The oxygen absorbing and desorbing capability of the composite oxide may be measured by the system (TPR Measuring System manufactured by SANTOKU METAL INDUSTRY CO., LTD.) described in and shown in Fig. 1 of T. Murota, T. Hasegawa, S. Aozasa, Journal of Alloys and Compounds, 193 (1993) p298. Specifically, 1 g of a sample is charged

in a quartz tube installed in a tubular furnace, and heated up to 200 to 1000 °C over 1 hour in the stream of a 10 % hydrogen gas diluted with an argon gas at 0.1 atm. The oxygen from the sample is reacted with the hydrogen to become H₂O, and the amount of thus generated H₂O is measured by sensing the difference between H₂O and the hydrogen gas in thermal conductivity at the thermal conductivity sensing portion of the gas chromatograph. Therefore, the total amount of oxygen desorbed up to 600°C is determined by the TPR curve drawn from the amounts of oxygen at each temperature.

For the purpose of demonstrating that the reduction ratio of the composite oxide of the present invention results in superior oxygen absorbing and desorbing capability, the relationship between the reduction ratio of Ce⁴⁺ in the composite oxide of the present invention into Ce³⁺ when the composite oxide is held at 600°C under a reducing atmosphere and the oxygen desorbing capability is shown in Fig. 1.

The conventional composite oxide containing cerium does not have the high degree of solid solution and the excellent reduction ratio at low temperatures, which properties are characteristic to the composite oxide of the present invention. This is believed to be attributed

to the fact that the conventional composite oxide containing cerium is prepared from the starting material solution which does not contain the particular amount of tetravalent cerium ions, and that the conventional composite oxide is prepared without the particular compositional adjustment and the particular calcining steps. For example, when zirconium and hafnium are precipitated from an acid aqueous solution containing zirconium and hafnium by neutralization with alkali, the precipitation is started near pH 2 and completed by pH 4. On the other hand, when cerium is precipitated from an aqueous solution of trivalent cerium by adding an alkali compound to the solution, the precipitation is started barely at pH 4 to 6, and is not completed up until pH 6 or higher. Accordingly, when an aqueous solution of cerium and a mixed salt of zirconium and hafnium is coprecipitated with an alkali compound for producing a precipitated composite salt, zirconium and hafnium precipitate first, and then cerium precipitates later. Thus, it is hard to obtain a precipitated composite salt having a uniform composition, and mixed hydroxides of cerium and zirconium along with hafnium are obtained. This is believed to be one of the reasons for the difference between the present invention and the prior

art.

The composite oxide of the present invention is easily prepared, for example, by the method of the present invention to be described later. However, it may also
5 be prepared, in some cases, only by the oxidizing calcination and without the reducing calcination to be described later, when the mixing ratio of cerium, zirconium, and hafnium, and the conditions for calcination are suitably selected.

10 In the first and second methods of the present invention, step (a) of precipitating a composite salt from a starting material solution containing the particular cerium ions, zirconium ions, and hafnium ions is first carried out. It is necessary that 85 to 100
15 weight %, preferably 90 to 100 weight % of the cerium ions contained in the starting material solution is tetravalent. By employing the starting material solution containing the particular ratio of tetravalent cerium ions for preparing the precipitate of the
20 composite salt, and subjecting the resulting precipitate to the particular calcination steps to be described later, a composite oxide with the desired, high degree of solid solution can be obtained. This is because the tetravalent cerium ions will only be dissolved in a strong

acid of pH 2 or lower, and will form a precipitate by neutralization with alkali around pH 2, so that the tetravalent cerium ions will behave in the similar way to the zirconium and hafnium ions contained in the starting material solution in dissolving and precipitating. Therefore, when the precipitate is formed through coprecipitation from a mixed solution of cerium, zirconium, and hafnium by neutralization with alkali, the precipitate is very likely to be a composite hydroxide wherein cerium, zirconium, and hafnium are uniformly integrated. It is believed that the degree of solid solution in the crystal phase of the composite oxide can be made more close to that of the complete solid solution by improving the uniformity of cerium, zirconium, and hafnium in the precipitate, adjusting the composition to the particular composition, and subjecting the precipitate to the particular calcinations.

The starting material solution containing the cerium ions, zirconium ions, and hafnium ions may be prepared by mixing a solution of a cerium salt containing 85 to 100 weight % tetravalent cerium ions, an aqueous solution of a nitrate of zirconium (or an aqueous solution of zirconyl nitrate), and an aqueous solution of a nitrate

of zirconium containing hafnium.

The solution of a cerium salt containing 85 to 100 weight % tetravalent cerium ions may be prepared by the following methods:

5 (1) a method including the steps of neutralizing a commercially available aqueous solution of cerous nitrate with aqua ammonia to form cerous hydroxide; adding hydrogen peroxide to the solution to oxidize the trivalent cerium ions to tetravalent; heating and
10 boiling the resulting solution containing the precipitate for decomposing and removing the residual hydrogen peroxide to precipitate ceric hydroxide; and dissolving the resulting precipitate in concentrated nitric acid to obtain an aqueous solution of tetravalent
15 cerium salt,

(2) a method including the steps of neutralizing a commercially available aqueous solution of cerous nitrate with aqua ammonia to form cerous hydroxide; filtering the resulting solution through a filter device
20 such as a filter press to obtain a cake of precipitate; placing the cake of precipitate in a flat-bottom vessel and heating at 100 to 150°C for 5 to 20 hours in the air for drying to oxidize the trivalent cerium ions into tetravalent; and dissolving the resulting cake of ceric

hydroxide in concentrated nitric acid to obtain an aqueous solution of tetravalent cerium salt, or

(3) a method including the steps of charging a commercially available aqueous solution of cerous nitrate in an electrolytic cell for electrolytic oxidation; and applying the electric current to anodically oxidize the trivalent cerium ions to tetravalent, thereby obtaining an aqueous solution of ceric nitrate.

10 The content of the tetravalent cerium ions in the solution of cerium salt may be measured, for example, by oxidation-reduction titration using potassium permanganate.

In preparing the starting material solution, for the purpose of improving the stability of the resulting composite oxide at high temperatures, a solution containing ions of other metals may optionally be admixed, such as titanium ions, tungsten ions, nickel ions, copper ions, iron ions, aluminum ions, silicon ions, beryllium ions, magnesium ions, calcium ions, strontium ions, barium ions, ions of rare earth metals other than cerium, or mixtures thereof.

The concentration of the cerium ions, zirconium ions, and hafnium ions together in the starting material

solution is preferably 30 to 200 g/liter, more preferably 50 to 100 g/liter in terms of oxides (tetravalent). The mixing ratio of cerium ions, zirconium ions, and hafnium ions, and optionally the ions of other metals to be added, if necessary, may suitably be selected so that the composition of the metals in the composite oxide to be obtained conforms to the composition of the composite oxide of the present invention. Specifically, it is preferred to mix each ion to have the mixing ratio of $\text{CeO}_2 : \text{ZrO}_2 : \text{HfO}_2 : \text{oxide of other metals} = 17-76.9 : 23-63 : 0.01-20 : 0-10$ by weight in terms of oxides.

Precipitation of a composite salt from the starting material solution may be effected by adding an alkali compound to the starting material solution to coprecipitate the metal ions. The alkali compound is preferably an aqueous solution of ammonia and/or an ammonia gas, since the requisite metal ions, namely, cerium ions (85 to 100 weight % of these are tetravalent), zirconium ions, and hafnium ions together start to precipitate near pH 2. When an aqueous solution of ammonia is used, it is preferred to set its concentration to 0.1 to 5 N, more preferably to 0.2 to 3 N. Further, the amount of the aqueous solution of ammonia to be added is preferably set so that the mixing ratio of the starting

material solution to the aqueous solution of ammonia is
1 : 1 to 1 : 10. When the aqueous solution of ammonia
is used, the precipitated composite salt to be obtained
is, for example, a composite hydroxide. On the other
5 hand, when an ammonia gas is used, the precipitated
composite salt to be obtained is, for example, a hydrated
composite oxide or a composite hydroxide.

The precipitated composite salt obtained above may
be subjected to filtration through an ordinary filter
10 device such as a filter press, or may be subjected to
decantation to reduce the water content. If necessary,
hydrothermal treatment or drying may be carried out.
Further, in the second method of the present invention
to be described later, the precipitated composite salt
15 may be subjected to the calcination step after a carbon
source or the like as a reducing agent is added to the
composite salt. The hydrothermal treatment may be
carried out in an ordinary autoclave preferably at 100
to 135°C for 1 to 5 hours. The drying may be carried out
20 preferably at a temperature lower than 250°C, but may
otherwise be carried out together in the calcination step
in the same furnace, for example, in a spray dryer type
furnace.

In the first method of the present invention, step

(b-1) of subjecting the precipitated composite salt obtained in step (a) to oxidizing calcination under the oxidizing atmosphere is carried out to obtain an oxidized, calcined product. The oxidizing atmosphere may be, for example, the air, a gas with oxygen partial pressure, or an oxygen gas atmosphere. The oxidizing calcination may be carried out preferably at 250°C or higher, more preferably at 300 to 1000°C, the most preferably at 600 to 1000°C, for 1 to 10 hours.

10 In the first method of the present invention, step (b-2) of subjecting the oxidized, calcined product obtained in step (b-1) at least once to reducing calcination followed by oxidizing calcination is carried out, thereby obtaining the composite oxide mentioned
15 above. With this step (b-2), the composite oxide of which degree of solid solution is not lower than 70 %, and which exhibits excellent reducing property at low temperatures is obtained. It is usually preferred to carry out the reducing calcination followed by oxidizing
20 calcination for 1 to 3 cycles.

The reducing calcination in step (b-2) may be carried out, for example, by a method including the steps of charging the calcined product obtained in step (b-1) in a vacuum furnace; evacuating the furnace; introducing

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a reducing gas such as a hydrogen gas and carbon monoxide into the furnace; and calcining the product under the reducing atmosphere preferably at 400 to 1000 °C, more preferably at 500 to 1000 °C, for 0.1 to 10 hours. The
5 reducing calcination may be carried out in the stream of a reducing gas, which may have been diluted with an inert gas. The concentration of the reducing gas, when diluted with an inert gas, is preferably 1 % or higher. This reducing calcination may be carried out under the
10 calcining conditions mentioned above with the reducing gas even after the composite oxide is put to use, for example, as a co-catalyst incorporated in a catalyst for purifying exhaust gases.

The reducing calcination in step (b-2) may be carried
15 out after a reducing agent such as a carbon source is admixed with the calcined product obtained in step (b-1). When the carbon source is admixed with the calcined product, the reducing calcination is carried out preferably at 800 to 1300 °C for 1 to 10 hours. The carbon
20 source may preferably be activated carbon, graphite powders, charcoal powders, soot, or mixtures thereof, and in particular in the form of fine powders of 100 mesh or smaller. Further, the carbon source may also be a solid substance which does not contain inorganic

substances such as organic oils, paraffin, organic acid,
tar, pitch , oil and fat, or mixtures thereof; or an
organic substance in the form of a solution obtained by
dissolving an organic substance in a solvent such as
5 kerosene. The organic substance is particularly
preferred since it also contains a hydrogen source and
is able to reduce the tetravalent cerium more securely.
The amount of the carbon source to be mixed is preferably
1 to 1.5 equivalent of the amount of cerium contained
10 in the calcined product obtained in step (b-1). The
reducing calcination incorporating the reducing agent
may be carried out under the reducing atmosphere or under
a non-oxidizing atmosphere such as an inert atmosphere,
and may also be carried out, in some cases, under a
15 particular oxidizing atmosphere such as in the air. When
the reducing calcination incorporating the reducing
agent is carried out in the air, the reducing calcination
is effected until the reducing agent is completely
consumed, and by continuing the calcination, the
20 oxidizing calcination is then effected. Therefore, the
reducing calcination in step (b-2) and the following
oxidizing calcination to be described later can be
carried out under the same atmosphere, preferably
successively. The reducing calcination incorporating

the reducing agent under an inert atmosphere or in the air is preferably carried out at 600 to 1000°C, more preferably 800 to 1000°C, for 1 to 10 hours.

Upon carrying out the reducing calcination in step (b-2), it is preferred to remove in advance any impurities attached to the calcined product obtained in step (b-1). Such impurities may be removed by a method including the steps of charging the calcined product obtained in step (b-1) in a vacuum furnace; evacuating the furnace; introducing an oxygen gas into the furnace; and holding preferably at 200 to 1000°C for 0.5 to 5 hours.

In step (b-2), the oxidizing calcination following the reducing calcination may preferably be carried out at 600 to 850°C for 0.5 to 10 hours, after evacuating the furnace again following the reducing calcination to remove the residual reducing gas, and applying the oxidizing atmosphere similar to the one in step (b-1) to the furnace. Alternatively, in the presence of the reducing agent mentioned above, the reducing calcination and the oxidizing calcination may be carried out under the same atmosphere.

In the second method of the present invention, step (b) of subjecting the precipitated composite salt obtained in step (a) at least once to reducing calcination

followed by oxidizing calcination is carried out. With this second method, a composite oxide having the particular degree of solid solution and exhibiting the excellent reducing property at low temperatures is
5 obtained. It is usually preferred to carry out the reducing calcination followed by oxidizing calcination for 1 to 3 cycles.

The reducing calcination in step (b) may be carried out by:

10 (1) calcining the precipitated composite salt obtained in step (a) under a reducing atmosphere;

(2) incorporating a reducing agent such as a carbon source into the precipitated composite salt obtained in step (a), and subjecting the composite salt with the
15 reducing agent to non-oxidizing calcination under a non-oxidizing atmosphere; or

(3) incorporating a reducing agent such as a carbon source into the precipitated composite salt obtained in step (a), and calcining the composite salt with the
20 reducing agent under a particular oxidizing atmosphere such as in the air.

In step (b), the reducing calcination by the method (1) mentioned above may be carried out by calcining the precipitated composite salt obtained in step (a) at 600

to 1000°C, preferably at 800 to 1000°C, for 0.1 to 10 hours under the atmosphere similar to the reducing atmosphere for step (b-2) in the first method of the present invention.

5 For the purpose of carrying out the reducing calcination in step (b) by the method (2) or (3) mentioned above, the reducing agent may be incorporated into the precipitated composite salt obtained in step (a) by incorporating the reducing agent in the starting
10 material solution; by adding the reducing agent during the preparation of the precipitated composite salt; or by mixing the reducing agent with the precipitated composite salt after the preparation thereof. In particular, for mixing the reducing agent with the
15 precipitated composite salt after preparation thereof, it is preferred to mix the reducing agent with the precipitated composite salt in the form of a slurry, followed by drying.

The reducing agent may preferably be the ones listed
20 above as the examples of the carbon source. The content of the carbon source is preferably 1 to 50 g, more preferably 2 to 30 g in terms of carbon per 100 g of cerium (weight in terms of CeO_2) in the starting material solution or in the precipitated composite salt. Further,

it is preferred to mix the carbon source with the composite salt by a homogenizer to prepare a homogeneous mixture.

In the method (2) mentioned above, "the non-oxidizing
5 calcination under a non-oxidizing atmosphere" means, for example, to calcine the precipitated composite salt containing the reducing agent in a nitrogen gas or an inert gas so that it will not be oxidized under a non-oxidizing atmosphere. The non-oxidizing
10 calcination may preferably be carried out at 600 to 1000°C, more preferably at 800 to 1000°C, for 1 to 10 hours.

In the method (3) mentioned above, the reducing calcination is effected until the reducing agent is completely consumed, and subsequently the oxidizing
15 calcination is effected. Therefore, the oxidizing calcination following the reducing calcination in step (b) can be carried out under the same atmosphere, preferably successively. The calcination by the method
20 (3) may be carried out preferably at 600 to 1000°C, more preferably at 800 to 1000°C, for 1 to 10 hours.

In step (b), the oxidizing calcination following the reducing calcination under the reducing atmosphere according to the method (1) or under the non-oxidizing atmosphere according to the method (2) mentioned above,

may be carried out by calcination after evacuating the furnace to remove the residual gas and applying the oxidizing atmosphere similar to the one in step (b-1); or by calcination after or during introduction of an oxidizing gas without evacuating the furnace, when the reducing calcination was effected by non-oxidizing calcination under the inert gas atmosphere. The oxidizing calcination may be carried out preferably at 600 to 1000°C, more preferably 800 to 1000°C, for 1 to 10 hours.

The composite oxide of the present invention has the particular composition containing cerium, zirconium, and hafnium as the requisite metals, has the degree of solid solution of not lower than 70 %, and exhibits excellent reducing property when it is held at 600 °C under a reducing atmosphere. Accordingly, the present composite oxide has the oxygen absorbing and desorbing capability superior to that of the conventional cerium-zirconium composite oxide, and is remarkably useful as a co-catalyst or functional ceramics and the like. Further, in the method of the present invention, the particular amount of tetravalent cerium ions are contained as the cerium material, and the particular calcining step is carried out. Accordingly, the

composite oxide of the present invention can easily be prepared.

Examples

The present invention will now be explained in more
5 detail with reference to Examples and Comparative
Examples, but the present invention is not limited
thereto.

Example 1

290 ml of an aqueous solution of cerous nitrate
10 prepared by dissolving high purity cerous nitrate
(manufactured by SANTOKU METAL INDUSTRY CO., LTD. with
a purity 99.9%) in water to have the concentration of
100 g/liter in terms of cerium oxide (CeO_2) was charged
in a beaker. While stirring this solution, a mixed
15 solution prepared by diluting 48 ml of concentrated aqua
ammonia and 12 ml of hydrogen peroxide (at the
concentration of 35 %) with 336 ml of water was
continuously charged into the beaker to precipitate
cerium in the form of a hydroxide and simultaneously
20 oxidize the hydroxide, thereby forming ceric hydroxide.
After that, the solution containing the precipitate was
heated beyond 75°C or boiled, and continuously stirred
for additional 2 hours to decompose and remove the
residual hydrogen peroxide. After the completion of the

precipitation, the supernatant was removed by
decantation, and 52 ml of concentrated nitric acid (at
the concentration of 66 %) was charged to dissolve the
precipitate, thereby obtaining 312 ml of a ceric nitrate
5 solution at the concentration of 93 g/liter in terms of
cerium oxide (CeO_2). This solution was subjected to
oxidation-reduction titration using potassium
permanganate. As a result, it was revealed that the
ratio of tetravalent cerium ions to the total amount of
10 cerium contained in the solution was 99 weight %.

This solution was mixed with 841 ml of an aqueous
solution of zirconium nitrate prepared by diluting a
zirconium nitrate solution (manufactured by DAIICHI
KIGENSO KOGYO CO., LTD. with a purity of 99.9 %) with
15 water into the concentration of 25 g/liter in terms of
zirconium oxide (ZrO_2) and 45 ml of an aqueous solution
of hafnium nitrate prepared by dissolving hafnium
nitrate (manufactured by WAKO PURE CHEMICAL INDUSTRIES,
LTD. with a purity of 97 %) in water to have the
20 concentration of 10 g/liter in terms of hafnium oxide
(HfO_2), thereby preparing an aqueous solution of mixed
nitrates having the concentration of 42.1 g/liter in
terms of oxides. Next, the thus obtained solution was
charged in a stirring vessel, to which separately

prepared 1.1 N aqua ammonia was added at the rate of 100 ml/min. to precipitate a composite salt containing cerium, zirconium, and hafnium. After the completion of the precipitation, the supernatant was removed, and
5 the precipitated composite salt was washed twice with pure water and filtered through a Nutsche type filter device. The resulting precipitated composite salt was charged in a furnace, and subjected to oxidizing calcination at 700°C for 5 hours in the air, thereby
10 obtaining 50.1 g of a cerium-zirconium-hafnium composite oxide. The composition of the metals in the resulting composite oxide is shown in Table 1.

Further, the composite oxide was measured of the XRD pattern by an X-ray diffraction apparatus manufactured
15 by RIGAKU CORPORATION (target: Cu, tube voltage: 40 KV, tube current: 40 mA, sampling interval: 0.010°, scanning rate: 4°/min.). The results are shown in Fig. 2. The lattice parameter on the (3, 1, 1) plane was 5.291 Å. The degree of solid solution of the obtained composite oxide
20 was calculated in accordance with the method for measuring the degree of solid solution of a composite oxide mentioned above. The results are shown in Table 2. Further, the composite oxide was measured of the oxygen desorbing capability per 1 g of the composite oxide,

the oxygen desorbing capability per 1 mol of the composite oxide calculated on the assumption that Ce in the composite oxide was CeO_2 , and the reduction ratio of Ce^{4+} to Ce^{3+} at 600 °C, in accordance with the method for measuring the oxygen desorbing capability and the method for measuring the reduction ratio mentioned above. The results are shown in Table 2. The TPR curve obtained from these measurements was also shown in Fig. 4.

Examples 2 and 3

A composite oxide was prepared in the same way as in Example 1 except that the aqueous solution of ceric nitrate was prepared in the same way as in Example 1 so that the ratio of the tetravalent cerium ions in the aqueous solution of ceric nitrate was as shown in Table 2, and that the composition of the metals in the aqueous solution of the mixed nitrates used in Example 1 was adjusted so as to obtain a composite oxide having the composition of the metals shown in Table 1. The degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured and calculated in the same way as in Example 1. The results are shown in Table 2.

Example 4

290 ml of an aqueous solution of cerous nitrate

prepared by dissolving high purity cerium nitrate
(manufactured by SANTOKU METAL INDUSTRY CO., LTD. with
a purity of 99.9 %) in water to have the concentration
of 100 g/liter in terms of cerium oxide (CeO_2) was charged
5 in a beaker. While stirring this solution, 337 ml of
2N aqua ammonia was added to the solution to precipitate
cerous hydroxide. After the completion of the
precipitation, the stirring was continued for 30 minutes,
and then the solution was left stand still. Subsequently,
10 the resulting precipitate was washed twice by
decantation, and filtered through a Nutsche type filter
device. The resulting cake of the precipitate was placed
in a ceramic vessel, and dried by heating at 120 °C for
5 hours in the air in a drying furnace to oxidize the
15 trivalent cerium to tetravalent, thereby obtaining ceric
hydroxide. Next, this hydroxide was dissolved in 150
ml of nitric acid diluted 1 : 1 with water, thereby
obtaining 170 ml of an aqueous solution of ceric nitrate
having the concentration of 170 g/liter in terms of cerium
20 oxide (CeO_2). This aqueous solution was subjected to the
same analysis as in Example 1 to reveal that the ratio
of tetravalent cerium ions to the total amount of cerium
contained in the solution was 98 weight %.

This solution was mixed with 878 ml of the aqueous

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solution of zirconium nitrate and 45 ml of the aqueous
solution of hafnium nitrate, both prepared in Example
1, thereby preparing an aqueous solution of mixed
nitrates having the concentration of 45.7 g/liter in
5 terms of oxides. Subsequently, 49.8 g of a cerium-
zirconium-hafnium composite oxide was obtained in the
same way as in Example 1. The composition of the metals
contained in the resulting composite oxide is shown in
Table 1. The degree of solid solution, the reduction
10 ratio, the oxygen desorbing capabilities of the
composite oxide were measured and calculated in the same
way as in Example 1. The results are shown in Table 2.

Examples 5 to 7

A composite oxide was prepared in the same way as in
15 Example 1 except that the aqueous solution of ceric
nitrate was prepared in the same way as in Example 1 so
that the ratio of the tetravalent cerium ions in the
aqueous solution of ceric nitrate was as shown in Table
2, and that the composition of the metals in the aqueous
20 solution of the mixed nitrates used in Example 1 was
adjusted so as to obtain a composite oxide having the
composition of the metals shown in Table 1. The degree
of solid solution, the reduction ratio, and the oxygen
desorbing capabilities of the resulting composite oxide

were measured and calculated in the same way as in Example 1. The results are shown in Table 2.

Example 8

The precipitated composite salt prepared in Example 1 was placed in a vacuum furnace, which was then evacuated. A pure oxygen gas was introduced into the furnace, and the furnace was heated to 900°C and held for 1 hour to remove the impurities attached to the composite salt. After that, the furnace was cooled down to 100°C and evacuated to remove the oxygen gas, into which furnace a 10 % hydrogen gas diluted with argon was then introduced. The precipitated composite salt was subjected to reducing calcination at 1000°C for 5 hours. Subsequently, the furnace was cooled down to 600°C and evacuated, into which an oxygen gas was introduced. The precipitated composite salt was subjected to oxidizing calcination at 600°C for 5 hours, thereby obtaining a composite oxide. The composition of the metals contained in the resulting composite oxide is shown in Table 1. Further, the degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured and calculated in the same way as in Example 1. The results are shown in Table 2.

Example 9

146 ml of an aqueous solution of ceric nitrate having the concentration of 200 g/liter in terms of cerium oxide (CeO_2) prepared in the same way as in Example 1 was mixed with 55 ml of an aqueous solution of zirconium nitrate prepared by diluting a zirconium nitrate solution (manufactured by DAIICHI KIGENSO KAGAKU KOGYO CO., LTD. with a purity of 99.9 %) with pure water into the concentration of 25 g/liter in terms of zirconium oxide (ZrO_2) and 24 ml of an aqueous solution of hafnium nitrate prepared by dissolving hafnium nitrate (manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD. with a purity of 99.5 %) in pure water to have the concentration of 10 g/liter in terms of hafnium oxide (HfO_2). Further, pure water was added to the mixture so that the final volume of the solution was 1 liter, thereby preparing an aqueous solution of mixed nitrates having the concentration of the composite oxide of 50 g/liter. To this solution, 1.5 g of activated carbon powders (manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD.: special grade) were added and mixed. To 1 liter of the solution obtained above, 1 liter of a separately prepared 1.2 N aqueous solution of ammonia was immediately added and mixed, thereby precipitating a composite salt containing a

carbon source. The resulting precipitate was washed by decantation, and then filtered through a Nutsche type filter device. Next, the precipitated composite salt thus collected was washed with 1 liter of pure water for 5 10 minutes and filtered. After this treatment was repeated twice, the precipitated composite salt was placed in a crucible, and subjected to reducing calcination at 700°C for 2 hours in a muffle furnace in the stream of a nitrogen gas (non-oxidizing calcination) 10 and to oxidizing calcination at 700°C for 10 hours in the stream of air, thereby obtaining 50 g of a composite oxide containing cerium, zirconium, and hafnium. The composition of the metals contained in the resulting composite oxide is shown in Table 1. Further, the degree 15 of solid solution, the reduction ratio, and the oxygen desorbing capabilities were measured and calculated in the same way as in Example 1. The results are shown in Table 1.

Example 10

20 Using an aqueous solution of ceric nitrate wherein the ratio of tetravalent cerium ions to all of the cerium ions in the aqueous solution was 98 weight %, an aqueous solution of mixed nitrates of cerium, zirconium, and hafnium was prepared in the same way as in Example 9.

To this aqueous solution of mixed nitrates, 930 ml of 1.2 N aqua ammonia was added to precipitate a composite salt, and the resulting precipitate was washed by decantation. The obtained slurry of the precipitate was heated to 80°C, to which 3 g of paraffin was added and homogenized by a homogenizer, thereby obtaining a precipitated composite salt containing paraffin. The precipitated composite salt thus obtained was placed in a ceramic plate, dried at 150°C for 2 hours in a muffle furnace in the stream of a nitrogen gas, and then transferred to an atmospheric furnace and calcined at 800°C for 5 hours, thereby preparing a composite oxide. Through this calcination, the reducing calcination and the oxidizing calcination were carried out in the same furnace. The composition of the metals in the resulting composite oxide is shown in Table 1. Further, the degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured in the same way as in Example 1. The results are shown in Table 2.

Comparative Example 1

A high purity cerous nitrate solution (manufactured by SANTOKU METAL INDUSTRY CO., LTD. with a purity of 99.9 %) was dissolved in water to prepare 290 ml of an

aqueous solution of cerium nitrate having the concentration of 100 g/liter in terms of cerium oxide (CeO_2). This aqueous solution was analyzed in the same way as in Example 1 to reveal that the ratio of tetravalent cerium ions to the total amount of cerium ions contained in this solution was 0 weight %.

This solution was mixed with 840 ml of an aqueous solution of zirconium nitrate prepared by diluting a zirconium nitrate solution (manufactured by DAIICHI KIGENSO KAGAKU KOGYO CO, LTD. with a purity of 99.9 %) with pure water into the concentration of 25 g/liter in terms of zirconium oxide (ZrO_2) and 45 ml of an aqueous solution of hafnium nitrate prepared by dissolving hafnium nitrate (manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD. with a purity of 99.5 %) in pure water to have the concentration of 10 g/liter in terms of hafnium oxide (HfO_2), thereby preparing an aqueous solution of mixed nitrates having the concentration of the composite oxide of 42.1 g/liter. Subsequently, a cerium-zirconium-hafnium composite oxide was prepared in the same way as in Example 1. The composition of the metals contained in the resulting composite oxide is shown in Table 1. Further, the degree of solid solution, the reduction ratio, the oxygen desorbing capabilities,

the X-ray diffraction, and the TPR curve of the resulting composite oxide were measured and calculated in the same way as in Example 1. The results of the degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities are shown in Table 2, the X-ray diffraction pattern is shown in Fig. 3, and the TPR curve is shown in Fig. 4, respectively.

Comparative Example 2

A composite oxide was prepared in the same way as in Comparative Example 1 except that the composition of the aqueous solution of the mixed nitrates used in Comparative Example 1 was adjusted so as to obtain a composite oxide having the composition of the metals as shown in Table 1. The degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured and calculated in the same way as in Example 1. The results are shown in Table 2.

Comparative Example 3

A composite oxide was prepared in the same way as in Comparative Example 1 except that an additional element was added to the aqueous solution of the mixed nitrates prepared in Comparative Example 1 so that the resulting composite oxide had the composition of the metals as shown

in Table 1. The degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured and calculated in the same way as in Example 1. The results are shown
5 in Table 2.

Comparative Example 4

A composite oxide was prepared by subjecting the composite oxide prepared in Comparative Example 1 to the reducing calcination and the oxidizing calcination in
10 the same way as in Example 8. The composition of the metals in the resulting composite oxide is shown in Table 1. Further, the degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the resulting composite oxide were measured and calculated
15 in the same way as in Example 1. The results are shown in Table 2.

Comparative Example 5

A composite oxide was prepared in the same way as in Example 1 except that an aqueous solution of ceric nitrate
20 was used, prepared in the same way as in Example 1 so that the content of the tetravalent cerium ions in the aqueous solution of the ceric nitrate was as shown in Table 2. The degree of solid solution, the reduction ratio, and the oxygen desorbing capabilities of the

resulting composite oxide were measured and calculated in the same way as in Example 1. The results are shown in Table 2.

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Table 1

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	Ratio of each metal based on total amount of Ce, Zr, and Hf in composite oxide (at%)			Content of Ce, Zr, and Hf in metals contained in composite oxide (wt%)	Content of metal other than Ce, Zr, and Hf in metals contained in composite oxide (wt%)		
	Ce	Zr	Hf		La	Ca	Nd
Example 1	48.94	50.43	0.63	100	-	-	-
Example 2	31.16	68.17	0.67	100	-	-	-
Example 3	57.40	42.25	0.35	100	-	-	-
Example 4	47.06	52.31	0.63	100	-	-	-
Example 5	48.77	50.60	0.63	99.04	0.96	-	-
Example 6	48.08	51.29	0.63	98.10	-	1.90	-
Example 7	49.08	50.32	0.60	97.90	-	-	2.10
Example 8	48.90	50.47	0.63	100	-	-	-
Example 9	49.84	49.81	0.35	100	-	-	-
Example 10	49.73	49.92	0.35	100	-	-	-
Comp.Ex.1	48.94	50.43	0.63	100	-	-	-
Comp.Ex.2	31.16	68.17	0.67	100	-	-	-
Comp.Ex.3	48.77	50.60	0.63	99.04	0.96	-	-
Comp.Ex.4	48.94	50.43	0.63	100	-	-	-
Comp.Ex.5	48.94	50.43	0.63	100	-	-	-

Table 2

7441X

	Ratio of Ce ⁴⁺ in starting material (%)	Degree of Solid Solution (%)	Reduction Ratio (%)	Oxygen Desorbing Capabilities	
				O ₂ mmol/mol (CeO ₂)	O ₂ μmol/g
Example 1	99	76	98	244	810
Example 2	98	83	99	270	605
Example 3	99	75	90	224	850
Example 4	98	71	91	228	730
Example 5	92	76	92	228	745
Example 6	91	76	95	237	760
Example 7	88	76	91	228	740
Example 8	99	76	98	245	810
Example 9	99	76	97	242	815
Example 10	98	71	99	242	815
Comp.Ex.1	0	12	27	68	225
Comp.Ex.2	0	15	42	114	256
Comp.Ex.3	0	18	28	72	235
Comp.Ex.4	0	58	62	157	521
Comp.Ex.5	80	52	59	148	489